

## ENGLISH TRANSLATION DOCUMENT

This application claims priority to a Chinese patent application entitled “Methods for Preparation from Carbonate Precursors the Compounds of Lithium Transition Metals Oxide” filed on November 19, 2002, having a Chinese Patent Application No. 02151991.9.

The following is the English Translation Document for the above referenced Chinese patent application.

# A Method for Preparation from Carbonate Precursors the Compounds of Lithium Transition Metals Oxide

## Abstract of Invention

This invention relates to methods for preparation from carbonate precursors the compounds of lithium transition metal oxides that include the following steps:

- (1) Formulate a solution which combines solution A that contains a mixture of ions of chromium, nickel, and manganese with solution B that contains  $\text{CO}_3^{2-}$  ions;
- (2) Combine solution A and solution B to react and form the carbonate precursor  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$ ;
- (3) Mix an even amount of  $\text{Li}_2\text{CO}_3$  with  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$ . Then calcinate in air at 500-800°C for 2 to 20 hours;
- (4) Cool and pulverize said calcinated material;
- (5) Calcinate at high temperature the pulverized calcinated material in air at 700 to 950°C for 2 to 30 hours;
- (6) Cool, ballmill, and sift to obtain the lithium transition metal oxide compound with the chemical formula  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ .

The  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{CO}_3$  that is prepared by the method of this invention has grain size distributed such that the average grain size is 10 $\mu\text{m}$  and its electrical capacity reaches 150mAh/g. It has a long cycle life and is suitable of use in lithium ion batteries.

## Description

### A Method for Preparation from Carbonate Precursors of the Compounds of Lithium Transition Metals Oxide from Carbonate Precursors

#### Field of Invention

This invention relates to a method to prepare a type of compound of lithium transitional metal oxide. In particular, it relates to the method of preparing carbonate precursors and compounds of lithium transitional metal oxide from carbonate precursors with excellent properties.

#### Background

Known commercialized lithium ion batteries use several types of transition metal oxide compounds such as lithium cobalt dioxide ( $\text{LiCoO}_2$ ), lithium nickel dioxide ( $\text{LiNiO}_2$ ), and lithium manganese dioxide ( $\text{LiMn}_2\text{O}_4$ ) etc. as the material for the positive electrode.  $\text{LiCoO}_2$  is the most commonly used material. Although the overall properties of  $\text{LiCoO}_2$  are the best, its cost is high and, due to its scarcity, the cost is likely to rise even higher. Its supply could even dry up. Therefore, many countries are focusing on manufacturing research of at least two of the following transition metals: Cobalt (Co), Nickel (Ni), and Manganese (Mn) as the basic ingredient for compounds of lithium transition metal oxide. Representative relevant work includes: 1. Zhaolin Lin et al. in J. Power Sources, 88-82 (1999) 416-419 discloses the synthesizing method for said oxide compound whose chemical

formula is  $\text{Li Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ; 2. Chinese Patent No. CN1271185A on October 25, 2000 discloses a method of preparation for a kind of additive ingredient of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$ .

The inventors of this invention researched and discovered that the materials prepared using the method described by Zhaolin, Lin, et al. (reference 1) have better properties such as the distribution of grain diameter, density, and electrochemical capacity, when compared with oxidized compounds prepared by mixing and combining the salts or hydroxide compounds of transition metal elements such as cobalt, nickel, and manganese and with salt of lithium and then decomposing the mixture thermally. However, in order to have said excellent properties in the oxidized compounds, the range of the distribution of the diameter for the spherical intermediate products formed using method reported by Zhaolin, Lin, et al in reference 1,  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$ , has to be narrow. This can only occur by strictly controlling the precipitation conditions which are difficult to accomplish in practice. The method in Chinese Patent No. CN1271185A (reference 2) spray mixes soluble salts, carbonates, or alkaline solutions of lithium and transition metals such as of cobalt, nickel, or manganese, and alkaline carbonates to obtain a crystal compound; then decompose thermally to obtain  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$  as the additive ingredient. However, this method is also difficult to implement since when the solubility volume of  $\text{Li}_2\text{CO}_3$  is close to  $10^{-3}$ , its solubility in water at normal temperature is 1 gram. It is inevitable that part of the  $\text{Li}_2\text{CO}_3$  is dissolved during the step when the crystal compounds are rinsed to remove the negative ions. This decreases the lithium content and results in the inability to obtain the amount calculated according to the formulas of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$ .

## Description of Invention

The objective of this invention is to eliminate the defects in existing methods, and to provide a method for preparing a compound of lithium transitional metal oxide with excellent properties by using  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$  or its hydroxide carbonate compound as a precursor, after decomposing it thermally with a lithium salt.

This invention can be realized by the following method:

The characteristics for a method to prepare from carbonate precursors the compounds of lithium transition metals oxide include the following steps:

- (1) Preparation of carbonate precursor
  - a. Formulation of a solution with an aqueous solution (hereinafter referred to as “solution A”) containing a mixture of at least two of the ions of the following metal elements (hereinafter “ $\text{Me}^{n+}$ ”): Cobalt (Co), Nickel (Ni), and manganese (Mn); and an aqueous solution containing ions of  $\text{CO}_3^{2-}$  (hereinafter “solution B”);
  - b. Mix, stir, and react solution A and solution B for several hours to obtain the  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$  precursor (including its hydroxide carbonate compound);

The specifications for reactions are: PH: 5 to 10, reaction temperature: 30 to 90°C, stirring speed: 20 to 120 revolutions, per minute, and reaction time: 2 to 30 hours;

(2) Formation of compound of lithium transition metal oxide

- a. Mix said  $\text{Li}_2\text{CO}_3$  and said  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$  evenly. Then calcinate in air in high temperature for several hours;
- b. Cool and pulverize of said material that has been calcinated;
- c. Again calcinate said pulverized calcinated material in air at high temperature for several hours;
- d. Cool, ballmill, and sift to obtain the compound of lithium transition metal oxide  $\text{Li Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ .

The specifications for reaction are: In step (2) a., the calcination is at 500 to 800°C for 2 to 20 hours. . In step (2) c., the calcination is at 700 to 950°C for 2 to 30 hours.

In step (1), the preferred ion concentration of solution A is 0.1 to 3.0 mol/l.  $\text{Me}^{n+}$  derives from at least one of the compounds from the following groups of materials: sulfates, nitrates, chlorides, acetates, other water soluble inorganic salts, and, other water soluble salts of organic acid. In step (1), a further preference is for solution A to contain at least one type of

additive ingredient from the group containing the ions of the following elements: Ca, Mg, Zn, Y, Ga, and In. The molar concentration of the additive component consists of 0 to 10% of the basic ingredients.

In step (1), the preferred  $\text{CO}_3^{2-}$  ion concentration of solution B is 0.1 to 3.0 mol/l. The  $\text{CO}_3^{2-}$  derives from at least one of the compounds from the following group of materials:  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ , other aqueous solution of carbonates, and other compatible water soluble salt containing  $\text{HCO}_3^-$ .

In step (1), the preferred PH level is adjusted by 1.0-6.0 mol/l of at least one aqueous solution (hereinafter “solution”) from the following groups: NaOH, KOH, and  $\text{NH}_3$ , and other alkaline aqueous solutions. Solutions A, B, and C are combined in a reactor which is continuously stirred.

In step (1), a further preference is for solution A to be a combination of the solutions of the salts of cobalt, nickel, and manganese; solution B is a  $\text{Na}_2\text{CO}_3$  solution; and solution C is a NaOH solution. The rate of flow is adjusted for the reaction to proceed at PH between 8 to 9 and the temperature is between 30-90°C.

Or, a further preference for step (1) is for solution A to be an aqueous solution of the combination of the sulfates salts of cobalt, nickel, and manganese; solution B to be  $(\text{NH}_4)_2\text{CO}_3$ ; and solution C be  $\text{NH}_3\cdot\text{H}_2\text{O}$

solution. The rate of flow is adjusted for the reaction to proceed at the PH level between 8 to 9 and the temperature is between 30 to 90°C.

A preference for step (2) is to first dry mix the  $\text{Li}_2\text{CO}_3$  with said  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$ , then wet mix with water or an organic solvent such as ethanol. The mixture is fully stirred and uniformly mixed. In step (2) a., the calcination is at 550 to 700°C, for 6 to 10 hours. In step (2) c., the calcination is at 750 to 900°C for 10 to 25 hours.

When compared with existing methods, this invention has the following advantages:

1. Calculations show that the material used can obtain the  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$  precursor or the hydroxide compounds of carbonates, which, when decompose thermally with  $\text{Li}_2\text{O}_3$  can produce said oxidized compound,  $\text{Li Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ . This is possibly due to the fact that lithium is fully mobile and nickel, cobalt, and manganese can be rearranged. This final product has a stable chemical composition and structure.
2. The technology is easy to control. Unlike the method used by Zhaolin, Lin, et al in reference 1, which, although it is good for the reactivity for intermediate bi-products, the hydroxides of compounds of nickel, cobalt and manganese, to be spherically shaped, the conditions for achieving this result cannot be easily controlled.



3. Strictly speaking, under alkaline conditions, the precursor product is the hydroxide salt of  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$ . When this product decomposes at high temperature, since its outward appearance is not spherical, and carbonates and hydroxide chemicals have different decomposition characteristics, the decomposition matter has crystalline defects and a large number of minute internal holes. Therefore its excellent qualities include: a comparatively larger volume, a long useable lifespan, and a narrow distribution of grain diameter.

#### Description of Attached Figures

Figure 1 is the photograph at 1000x magnification of an example of the  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$  precursor made by an embodiment of this invention.

Figure 2 is an example of the grain size distribution of the  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$  precursor made by of an example of an embodiment of invention.

Figure 3 shows the electrical discharge curves of a lithium ion battery made made with  $\text{Li Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  by an example of an embodiment of this invention and  $\text{Li}_2\text{CO}_2$ .

Figure 4 is a curve of the cycle characteristics of a lithium ion battery made with  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  by an example of an embodiment of this invention.

#### Method of Implementation

The following, together with the attached figure explains this invention in detail.

As an example, to form the chemical  $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{CO}_3$ , the calculated formula combines 1.0 mol/l of an aqueous solution of sulfate solution of a combination of cobalt, nickel, and manganese, 1.00 mol/l of aqueous solution of NaOH, and 1.0 mol/l of aqueous solution of  $\text{Na}_2\text{CO}_3$  and add into reactor. The reaction temperature is kept at  $45^\circ\text{C}$ , and the solution PH level is kept between 8.5 to 9. The mixture is stirred at 40 revolutions per minute for the 10 hours of reaction time. The  $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{CO}_3$  precursor is obtained after filtering, washing, and drying. The scanning electron micrograph in Figure (1) shows that this precursor is not spherically shaped, of even size and distributed and not clustered. Figure (2) shows that the range of grain size distribution is narrow with average grain size as  $10\mu\text{m}$ .

As an example, to form the chemical  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ , a calculated amount of  $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{CO}_3$  precursor and  $\text{Li}_2\text{CO}_3$  are added in. The dry materials are first mixed together, then water is added and the ingredients are combined with a wet mix method, fully stirring the mixture to combine evenly before transferring to the reactor. The mixture is calcinated at  $550^\circ$  for 6 hours. It is then cooled and pulverized. The material is then again calcinated at  $850^\circ\text{C}$  for 20 hours. It is then cooled, and ballmill to make  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ . In the resulting product, the range of the distribution of grain size is narrow and the average grain size in  $10\mu\text{m}$ . A customary method is used to make a lithium ion battery with said

$\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  Its electrical properties are compared with a  $\text{Li}_2\text{CoO}_2$  battery. In Figure (3), the curves showing the discharge of the two batteries can be compared. Curve 2 and Curve 1 shows the discharge characteristics of an example of a battery made from an embodiment of this invention and a  $\text{Li}_2\text{CoO}_2$  battery, respectively. The graphs show that the discharge capacity of the battery made from the compound of lithium transition metal oxide prepared from an embodiment of this invention is high, reaching to 720 minutes. The electrical capacity is calculated to be 150mAh/g. Also, the midpoint voltage of the discharge platform is near that of the  $\text{Li}_2\text{CoO}_2$  battery. Its cycling life also reaches 500 times. Since the amount of cobalt used is low but the properties of the battery is not reduced, the compounds of lithium transition metals oxide from carbonate precursors made from this invention is new, innovative, has distinctive characteristics, and has widespread application.

## CLAIMS

1. A method for preparation from carbonate precursors the compounds of lithium transition metals oxide. Its characteristics include the following steps:

(1) Preparation of carbonate precursor

a. Formulation of a solution with an aqueous solution (hereinafter referred to as “solution A”) containing a mixture of at least two of the ions of the following metal elements (hereinafter “ $Me^{n+}$ ”): Cobalt (Co), Nickel (Ni), and manganese (Mn); and an aqueous solution containing ions of  $CO_3^{2-}$  (hereinafter “solution B”);

b. Mix, stir, and react solution A and solution B for several hours to obtain the  $Ni_{1-x-y}Co_xMn_yCO_3$  precursor (including its hydroxide carbonate compound);

The specifications for reactions are: PH: 5 to 10, reaction temperature: 30 to 90°C, stirring speed: 20 to 120 revolutions, per minute, and reaction time: 2 to 30 hours;

(2) Formation of compound of lithium transition metal oxide

- a. Mix said  $\text{Li}_2\text{CO}_3$  and said  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$  evenly. Then calcinate in air in high temperature for several hours;
- b. Cool and pulverize said material that has been calcinated;
- c. Again calcinate said pulverized calcinated material in air at high temperature for several hours;
- d. Cool, ballmill, and sift to obtain the compound of lithium transition metal oxide  $\text{Li Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ .

The specifications for reaction are: In step (2) a., the calcination is at 500 to 800°C for 2 to 20 hours. . In step (2) c., the calcination is at 700 to 950°C for 2 to 30 hours.

2. The method for preparation of compounds of lithium transition metals oxide from carbonate precursors in Claim 1 wherein in step (1), the ion concentration of solution A is 0.1 to 3.0 mol/l.  $\text{Me}^{n+}$  derives from at least one of the compounds from the following groups of materials: sulfates, nitrates, chlorides, acetates, other water soluble inorganic salts, and, other water soluble salts of organic acid.
3. The method for preparation of compounds of lithium transition metals oxide from carbonate precursors in Claim 2 wherein in step (1), solution A contains at least one type of additive ingredient from the group containing the ions of the following elements: Ca, Mg, Zn, Y, Ga, and In.

The molar concentration of the additive component consists of 0 to 10% of the basic ingredients.

4. The method for preparation of compounds of lithium transition metals oxide from carbonate precursors in Claim 1 wherein in step (1), the  $\text{CO}_3^{2-}$  ion concentration of solution B is 0.1 to 3.0 mol/l. The  $\text{CO}_3^{2-}$  derives from at least one of the compounds from the following group of materials:  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ , other aqueous solution of carbonates, and other compatible water soluble salt containing  $\text{HCO}_3^-$ .
5. The method for preparation of compounds of lithium transition metals oxide from carbonate precursors in Claim 1 wherein in step (1), the PH level is adjusted by 1.0-6.0 mol/l of at least one aqueous solution (hereinafter "solution") from the following groups: NaOH, KOH, and  $\text{NH}_3$ , and other alkaline aqueous solutions. Solutions A, B, and C are combined in a reactor which is continuously stirred.
6. The method for preparation of compounds of lithium transition metals oxide from carbonate precursors in Claim 2, 4, or 5 wherein in step (1), solution A is a combination of the solutions of the salts of cobalt, nickel, and manganese; solution B is a  $\text{Na}_2\text{CO}_3$  solution; and solution C is a NaOH solution. The rate of flow is adjusted for the reaction to proceed at PH between 8 to 9 and the temperature is between 30-90°C.
7. The method for preparation of compounds of lithium transition metals oxide from carbonate precursors in Claim 2, 4, or 5

wherein in step (1), solution A is an aqueous solution of the combination of the sulfates salts of cobalt, nickel, and manganese; solution B to be  $(\text{NH}_4)_2\text{CO}_3$ ; and solution C be  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution. The rate of flow is adjusted for the reaction to proceed at the PH level between 8 to 9 and the temperature is between 30 to 90°C.

8. The method for preparation of compounds of lithium transition metals oxide from carbonate precursors in Claim 1 wherein in step (2), first dry mix the  $\text{Li}_2\text{CO}_3$  with said  $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y\text{CO}_3$ , then wet mix with water or an organic solvent such as ethanol. The mixture is fully stirred and uniformly mixed. In step (2)a., the calcination is at 550 to 700°C, for 6 to 10 hours. In step (2)c., the calcination is at 750 to 900°C for 10 to 25 hours